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# Glossy transfer-resistant composition comprising a block polymer

The present invention relates to a cosmetic composition for making up or caring for the skin, including the scalp, of both the human face and body, and human lips or integuments, for instance the hair, the eyelashes or the eyebrows, comprising a cosmetically acceptable organic liquid medium and a particular block polymer.

"Transfer-resistant" lip and skin makeup compositions are compositions that have the advantage of forming a deposit that does not transfer or that does not leave traces or marks, at least partially, on the supports with which they come into contact (glass, clothing, cigarette or fabrics).

Known transfer-resistant compositions are based on silicone resins and volatile silicone oils and, although having improved staying power properties, 20 have the drawback of leaving on the skin and the lips, after the volatile silicone oils have evaporated off, a film that becomes uncomfortable over time (sensation of drying out and of tautness) and is barely glossy.

However, women are nowadays seeking products, especially for colouring the lips or the eyelids, which are glossy while at the same time being transfer-

resistant.

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There is still a need for a cosmetic product that not only has good staying power, but is also transfer-resistant and glossy.

A method has been proposed in the prior art, in patent application WO-A-97/17057 from the company Procter & Gamble, for increasing the gloss and the comfort of transfer-resistant compositions, which consists in applying two compositions, one over the other. However, these products remain uncomfortable. In addition, the application of two compositions may be unacceptable for certain consumers.

The aim of the present invention is to propose a novel route for formulating a cosmetic

15 product, in particular a makeup product, which allows good "transfer-resistance" and gloss properties.

This product especially has the advantage of comprising only one composition, in contrast with the product of patent application WO-A-97/17057.

The product obtained according to the invention, especially when it is a product for the lips, has good properties of migration resistance, staying power and absence of a sensation of drying out.

up the skin and/or the lips and/or integuments,

One subject of the invention is a glossy, transfer-resistant composition for caring for or making

containing a film-forming linear block ethylenic polymer. The inventors have found, surprisingly, that the use of such a block polymer makes it possible to obtain a glossy, transfer-resistant composition. The composition according to the invention also has the advantage of having good staying power.

The composition of the invention may in particular constitute a haircare product or a makeup product for human body, lips or integuments having care and/or treating properties. It especially constitutes a lipstick or a lipgloss, an eyeshadow, attack to product, a mascara, an eyeliner, a product for artificially tanning the skin, an optionally tinted care or protecting cream, a hair-colouring product or a haircare product.

A subject of the invention is, more specifically, a cosmetic composition containing a cosmetically acceptable organic liquid medium and a film-forming linear ethylenic block polymer, the said polymer being such that, when it is in sufficient amount in the composition:

- the mean gloss at 20° of a deposit of the said composition, once spread onto a support, is greater than or equal to 30 out of 100, and
- 25 the transfer index is less than or equal to 40 out of 100.

Preferably, the composition according to the invention is a leave-in composition.

The invention also relates to a cosmetic composition comprising an organic liquid medium and at least one block polymer as described below.

## Mean gloss of the composition

The term "mean gloss" means the gloss as may be conventionally measured using a glossmeter by the following method.

A coat of between 50 μm and 150 μm in thickness of the composition is spread using an automatic spreader onto a Leneta brand contrast card of reference Form 1A Penopac. The coat covers at least the white background of the card. The deposit is left to dry for 24 hours at a temperature of 30°C, and the gloss at 20° is then measured on the white background using a Byk Gardner brand glossmeter of reference microTri-Gloss.

This measurement (between 0 and 100) is

repeated at least three times, and the mean gloss is
the mean of the at least three measurements taken.

The mean gloss of the composition measured at 20° is advantageously greater than or equal to 30, better still greater than or equal to 35, better still greater than or equal to 40, better still greater than or equal to 45, better still greater than or equal to

50 out of 100, better still greater than or equal to 55, and better still greater than or equal to 60.

Preferably, the mean gloss of the composition, once spread onto a support, measured at 60° is greater than or equal to 50, better still greater than or equal to 60, better still greater than or equal to 65, better still greater than or equal to 70, better still greater than or equal to 75, better still greater than or equal to 80, better still greater than or equal to 85 or better still greater than or equal to 90 out of 100.

The mean gloss at 60° is measured as follows. The gloss may be measured using a glossmeter, in a conventional manner, by the following method.

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15 A coat of between 50 μm and 150 μm in thickness of the composition is spread using an automatic spreader onto a Leneta brand contrast card of reference Form 1A Penopac. The coat covers at least the white background of the card. The deposit is left to 20 dry for 24 hours at a temperature of 30°C, and the gloss at 60° is then measured on the white background using a Byk Gardner brand glossmeter of reference microTri-Gloss.

This measurement (between 0 and 100) is

25 repeated at least three times, and the mean gloss is
the mean of the at least three measurements taken.

According to one embodiment, the mean gloss of the composition measured at 20° is preferably greater than or equal to 35, preferably 40, 45 or 50 out of 100, and/or the mean gloss of the composition measured at 60° is preferably greater than or equal to 65, 70 or 75 out of 100. In this embodiment, the composition advantageously constitutes a liquid lipstick.

# Transfer index of the composition

10 The transfer index of the composition according to the invention is preferably less than or equal to 40 out of 100. More preferably, the transfer index is less than or equal to 30, preferably less than or equal to 20, more preferably less than or equal to 15, preferably less than or equal to 10, preferably less than or equal to 5 out of 100, and preferably less than or equal to 2 out of 100.

The transfer index may be measured according to the following method.

A support (rectangle of 40 mm × 70 mm and 3 mm thick) of polyethylene foam that is adhesive on one of the faces, having a density of 33 kg/m³ (sold under the name RE40X70EP3 from the company Joint Technique Lyonnais Ind) is preheated on a hotplate

25 maintained at a temperature of 40°C in order for the surface of the support to be maintained at a

temperature of 33°C ± 1°C.

The composition is applied over the entire non-adhesive surface of the support, by spreading it using a fine brush to obtain a deposit of about 15 µm of the composition, while leaving the support on the hotplate, and the support is then left to dry for 30 minutes.

After drying, the support is bonded via its adhesive face onto an anvil 20 mm in diameter and equipped with a screw pitch. The support/deposit assembly is then cut up using a punch 18 mm in diameter. The anvil is then screwed onto a press (Statif Manuel Imada SV-2 from the company Someco) equipped with a tensile testing machine (Imada DPS-20 from the company Someco).

White photocopier paper of  $80 \text{ g/m}^2$  is placed on the bed of the press and the support/deposit assembly is then pressed on the paper at a pressure of 2.5 kg for 30 seconds. After removing the

- 20 support/deposit assembly, some of the deposit is transferred onto the paper. The colour of the deposit transferred onto the paper is then measured using a Minolta CR300 colorimeter, the colour being characterized by the L\*, a\*, b\* colorimetric
- 25 parameters. The colorimetric parameters  $L^*_0$ ,  $a^*_0$  and  $b^*_0$  of the colour of the plain paper used is determined.

The difference in colour  $\Delta E1$  between the colour of the deposit transferred relative to the colour of the plain paper is then determined by means of the following relationship.

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$$\Delta E1 = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$

Moreover, a total transfer reference is prepared by applying the composition directly onto a 10 paper identical to the one used previously, at room temperature (25°C), by spreading the composition using a fine brush and so as to obtain a deposit of about 15 µm of the composition, and the deposit is then left to dry for 30 minutes at room temperature (25°C). After drying, the colorimetric parameters L\*', a\*' and b\*' of the colour of the deposit placed on the paper, corresponding to the reference colour of total transfer, is measured directly. The colorimetric parameters L\*'0, a\*'0 and b\*'0 of the colour of the plain paper used are determined.

The difference in colour  $\Delta E2$  between the reference colour of total transfer relative to the colour of the plain paper are then determined by means of the following relationship.

$$\Delta E2 = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$

The transfer of the composition, expressed as a percentage, is equal to the ratio:

 $100 \times \Delta E1/\Delta E2$ 

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The measurement is performed on 4 supports in succession and the transfer value corresponds to the mean of the 4 measurements obtained with the 4

10 supports. The transfer index is equal to the mean of these four measurements.

The invention also relates to a process for making up the skin and/or the lips and/or integuments, which consists in applying to the skin and/or the lips and/or integuments the composition as defined above.

The composition according to the invention may be applied to the skin of both the face and the scalp and of the body, mucous membranes, for instance the lips and the inside of the lower eyelids, and integuments, for instance the eyelashes, the hair, the eyebrows, or even body hairs.

The invention also relates to the use of a block polymer in a sufficient amount in a cosmetic composition to impart gloss and transfer resistance to a deposit of the said composition.

The invention also relates to the cosmetic use of the composition defined above to improve the gloss of the makeup on the skin and/or the lips and/or integuments.

5 The composition advantageously contains a small proportion of oils conventionally used to impart gloss, these oils generally being tacky. The composition according to the invention advantageously contains less than 30%, less than 25%, less than 20% and better still less than 15% of at least one glossy oil.

The term "oil" means a compound that is immiscible with water in all proportions, and which is liquid at room temperature (25°C) and atmospheric pressure (760 mmHg).

The glossy oil has, for example, a molar mass ranging from 650 to 10~000 g/mol and preferably from 750 to 7500 g/mol.

The oil with a molar mass ranging from 650 to 20 10 000 g/mol may be chosen from:

- lipophilic polymers such as:
  - polybutylenes such as Indopol H-100 (molar mass or MM = 965 g/mol), Indopol H-300 (MM = 1340 g/mol) and Indopol H-1500 (MM = 2160 g/mol) sold or
- 25 manufactured by the company Amoco,
  - hydrogenated polyisobutylenes such as Panalane

H-300 E sold or manufactured by the company Amoco (M = 1340 g/mol), Viseal 20000 sold or manufactured by the company Synteal (MM = 6000 g/mol) and Rewopal PIB 1000 sold or manufactured by the company Witco (MM = 1000 g/mol),

- -- polydecenes and hydrogenated polydecenes such as:

  Puresyn 10 (MM = 723 g/mol) and Puresyn 150 (MM = 9200 g/mol) sold or manufactured by the company

  Mobil Chemicals,
- vinylpyrrolidone copolymers such as:
   vinylpyrrolidone/1-hexadecene copolymer, Antaron
   V-216 sold or manufactured by the company ISP (MM
  = 7300 g/mol),

#### - esters such as:

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- 15 linear fatty acid esters with a total carbon number ranging from 35 to 70, for instance pentaerythrityl tetrapelargonate (MM = 697.05 g/mol),
  - hydroxylated esters such as polyglyceryl-2
    triisostearate (MM = 965.58 g/mol),
    - aromatic esters such as tridecyl trimellitate (MM
      = 757.19 g/mol),
    - esters of branched  $C_{24}$ - $C_{28}$  fatty alcohols or fatty acids such as those described in patent
- application EP-A-0 955 039, and especially triisoarachidyl citrate (MM = 1033.76 g/mol),

pentaerythrityl tetraisononanoate (MM =
697.05 g/mol), glyceryl triisostearate (MM =
891.51 g/mol), glyceryl tris(2decyl)tetradecanoate (MM = 1143.98 g/mol),

- pentaerythrityl tetraisostearate (MM = 1202.02 g/mol), polyglyceryl-2 tetraisostearate (MM = 1232.04 g/mol) or pentaerythrityl tetrakis(2-decyl)tetradecanoate (MM = 1538.66 g/mol),
- silicone oils such as phenylsilicones, for instance
  10 Belsil PDM 1000 from the company Wacker (MM =
   9000 g/mol),
  - oils of plant origin, such as sesame oil (820.6 g/mol),
  - and mixtures thereof.

#### 15 Block polymer:

The composition according to the present invention contains at least one block polymer. The term "block" polymer means a polymer comprising at least two different blocks and preferably at least three

20 different blocks.

According to one embodiment, the block polymer of the composition according to the invention is an ethylenic polymer. The term "ethylenic" polymer means a polymer obtained by polymerizing monomers comprising an ethylenic unsaturation.

According to one embodiment, the block

polymer of the composition according to the invention is a linear polymer. In contrast, a polymer of non-linear structure is, for example, a polymer of branched, starburst or grafted structure, or the like.

According to one embodiment, the block polymer of the composition according to the present invention is a film-forming polymer. The term "film-forming" polymer means a polymer capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous film that adheres to a support and especially to keratin materials.

According to one embodiment, the block polymer of the composition according to the invention is a non-elastomeric polymer.

15 The term "non-elastomeric polymer" means a polymer which, when it is subjected to a constraint intended to stretch it (for example by 30% relative to its initial length), does not return to a length substantially identical to its initial length when the 20 constraint ceases.

More specifically, the term "non-elastomeric polymer" denotes a polymer with an instantaneous recovery  $R_i$  < 50% and a delayed recovery  $R_{2h}$  < 70% after having been subjected to a 30% elongation. Preferably, 25  $R_i$  is < 30% and  $R_{2h}$  < 50%.

More specifically, the non-elastomeric nature

of the polymer is determined according to the following protocol:

A polymer film is prepared by pouring a solution of the polymer in a Teflon-coated mould,

5 followed by drying for 7 days in an environment conditioned at 23 ± 5°C and 50 ± 10% relative humidity.

A film about 100  $\mu m$  thick is thus obtained, from which are cut rectangular specimens (for example using a punch) 15 mm wide and 80 mm long.

This sample is subjected to a tensile stress using a machine sold under the reference Zwick, under the same temperature and humidity conditions as for the drying.

The specimens are pulled at a speed of 15-50~mm/min and the distance between the jaws is 50~mm, which corresponds to the initial length  $(l_0)$  of the specimen.

The instantaneous recovery  $R_{\rm i}$  is determined in the following manner:

20 - the specimen is pulled by 30% ( $\epsilon_{max}$ ), i.e. about 0.3 times its initial length ( $l_0$ )

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- the constraint is released by applying a return speed equal to the tensile speed, i.e. 50 mm/min, and the residual elongation of the specimen is measured as a percentage, after returning to zero constraint  $(\epsilon_1)$ .

The percentage instantaneous recovery  $(R_i)$  is

given by the following formula:

$$R_i = (\epsilon_{max} - \epsilon_1)/\epsilon_{max}) \times 100$$

To determine the delayed recovery, the  $\mbox{percentage residual elongation of the specimen } (\epsilon_{2h}) \mbox{ is}$   $\mbox{measured, 2 hours after returning to zero constraint.}$ 

The percentage delayed recovery  $(R_{2h})$  is given by the following formula:

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chloromethylstyrene.

$$R_{2h} = (\epsilon_{max} - \epsilon_{2h})/\epsilon_{max}) \times 100$$

Purely as a guide, a block polymer according to one embodiment of the invention has an instantaneous recovery  $R_{\rm i}$  of 10% and a delayed recovery  $R_{\rm 2h}$  of 30%.

According to another embodiment, the block polymer of the composition according to the invention does not comprise any styrene units. The expression "polymer free of styrene units" means a polymer comprising less than 10%, preferably less than 5%, preferentially less than 2% and more preferentially less than 1% by weight i) of styrene units of formula  $-CH(C_6H_5)-CH_2-$  or ii) of substituted styrene units, for instance methylstyrene, chlorostyrene or

According to one embodiment, the block

polymer of the composition according to the invention is derived from aliphatic ethylenic monomers. The term "aliphatic monomer" means a monomer comprising no aromatic groups.

According to one embodiment, the block polymer is an ethylenic polymer derived from aliphatic ethylenic monomers comprising a carbon-carbon double bond and at least one ester group -COO- or amide group -CON-. The ester group may be linked to one of the two unsaturated carbons via the carbon atom or the oxygen atom. The amide group may be linked to one of the two unsaturated carbons via the carbon atom or the nitrogen atom.

According to one embodiment, the block

15 polymer comprises at least one first block and at least
one second block.

The term "at least one block" means one or more blocks.

It is pointed out that, in the text herein20 above and hereinbelow, the terms "first" and "second"
blocks do not in any way condition the order of the
said blocks in the polymer structure.

According to one embodiment, the block polymer comprises at least one first block and at least one second block that have different glass transition temperatures (Tg).

In this embodiment, the first and second blocks may be linked together via an intermediate segment with a glass transition temperature between the glass transition temperatures of the first and second blocks.

According to one embodiment, the block polymer comprises at least one first block and at least one second block linked together via an intermediate segment comprising at least one constituent monomer of the first block and at least one constituent monomer of the second block.

Preferably, the intermediate block is derived essentially from constituent monomers of the first block and of the second block.

The term "essentially" means at least 85%, preferably at least 90%, better still 95% and even better still 100%.

Advantageously, the intermediate segment comprising at least one constituent monomer of the 20 first block and at least one constituent monomer of the second block of the polymer is a random polymer.

According to one embodiment, the block polymer comprises at least one first block and at least one second block that are incompatible in the organic

25 liquid medium of the composition of the invention.

The term "mutually incompatible blocks" means

that the mixture formed from the polymer corresponding to the first block and from the polymer corresponding to the second block is not miscible in the liquid that is in major amount by weight contained in the organic

- liquid medium of the composition, at room temperature (25°C) and atmospheric pressure (10<sup>5</sup> Pa), for a contentof the polymer mixture of greater than or equal to 5%
  by weight, relative to the total weight of the mixture (polymers and major organic liquid), it being
- 10 understood that:
  - i) the said polymers are present in the mixture in a content such that the respective weight ratio ranges from 10/90 to 90/10, and that
- ii) each of the polymers corresponding to the first and second blocks has an average (weight-average or number-average) molecular mass equal to that of the block polymer ± 15%.

When the organic liquid medium comprises a mixture of organic liquids, in the case of two or more liquids present in identical mass proportions, the said polymer mixture is immiscible in at least one of them.

When the organic liquid medium comprises only one organic liquid, this liquid obviously constitutes the liquid that is in major amount by weight.

The term "organic liquid medium" means a medium containing at least one organic liquid, i.e. at

least one organic compound that is liquid at room
temperature (25°C) and atmospheric pressure (10<sup>5</sup> Pa).
According to one embodiment, the major liquid of the
organic liquid medium is a volatile or non-volatile oil

(fatty substance). Preferably, the organic liquid is
cosmetically acceptable (acceptable tolerance,
toxicology and feel). The organic liquid medium is
cosmetically acceptable, in the sense that it is
compatible with keratin materials, for instance the

oils or organic solvents commonly used in cosmetic
compositions.

According to one embodiment, the major liquid of the organic liquid medium is the polymerization solvent or one of the polymerization solvents of the block polymer, as are described below.

The term "polymerization solvent" means a solvent or a mixture of solvents. The polymerization solvent may be chosen especially from ethyl acetate, butyl acetate, alcohols such as isopropanol and ethanol, aliphatic alkanes such as isododecane, and mixtures thereof. Preferably, the polymerization solvent is a mixture of butyl acetate and isopropanol, or isododecane.

In general, the block polymer may be
25 incorporated into the composition to a high solids
content, typically greater than 10%, greater than 20%,

more preferably greater than 30% and more preferentially greater than 45% by weight relative to the total weight of the composition, while at the same time being easy to formulate.

Preferably, the block polymer comprises no silicon atoms in its skeleton. The-term "skeleton" means the main chain of the polymer, as opposed to the pendent side chains.

Preferably, the polymer according to the

invention is not water-soluble, i.e. the polymer is not

soluble in water or in a mixture of water and linear or

branched lower monoalcohols containing from 2 to 5

carbon atoms, for instance ethanol, isopropanol or

n-propanol, without pH modification, at an active

material content of at least 1% by weight, at room

temperature (25°C).

According to one embodiment, the block polymer has a polydispersity index I of greater than 2.

Advantageously, the block polymer used in the compositions according to the invention has a polydispersity index I of greater than 2, for example ranging from 2 to 9, preferably greater than or equal to 2.5, for example ranging from 2.5 to 8 and better still greater than or equal to 2.8, and especially ranging from 2.8 to 6.

The polydispersity index I of the polymer is

equal to the ratio of the weight-average mass Mw to the number-average mass Mn.

The weight-average molar mass (Mw) and number-average molar mass (Mn) are determined by gel permeation liquid chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

The weight-average mass (Mw) of the block polymer is preferably less than or equal to 300 000; it 10 ranges, for example, from 35 000 to 200 000 and better still from 45 000 to 150 000.

The number-average mass (Mn) of the block polymer is preferably less than or equal to 70 000; it ranges, for example, from 10 000 to 60 000 and better still from 12 000 to 50 000.

Each block of the block polymer is derived from one type of monomer or from several different types of monomer.

This means that each block may consist of a 20 homopolymer or a copolymer; this copolymer constituting the block may in turn be random or alternating.

The glass transition temperatures indicated for the first and second blocks may be theoretical Tg values determined from the theoretical Tg values of the constituent monomers of each of the blocks, which may be found in a reference manual such as the Polymer

Handbook, 3rd Edition, 1989, John Wiley, according to the following relationship, known as Fox's law:

$$1/Tg=\Sigma (\omega_i/Tg_i)$$
,

 $\mathbf{\sigma}_{i}$  being the mass fraction of the monomer i in the block under consideration and  $\mathbf{Tg}_{i}$  being the glass transition temperature of the homopolymer of the monomer i.

Unless otherwise indicated, the Tg values

10 indicated for the first and second blocks in the

present patent application are theoretical Tg values.

The difference between the glass transition temperatures of the first and second blocks is generally greater than 10°C, preferably greater than 15 20°C and better still greater than 30°C.

In particular, the block polymer comprises at least one first block and at least one second block such that the first block may be chosen from:

- a) a block with a Tg of greater than or equal to 40°C,
  - b) a block with a Tg of less than or equal to 20°C,
- c) a block with a Tg of between 20 and 40°C, and the second block can be chosen from a category

  a), b) or c) different from the first block.

In the present invention, the expression:

"between ... and ..." is intended to denote a range of values for which the limits mentioned are excluded, and "from ... to ..." and "ranging from ... to ..." are intended to denote a range of values for which the limits are included.

# a) Block with a Tg of greater than or equal to 40°C

The block with a Tg of greater than or equal to 40°C has, for example, a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C.

The block with a Tg of greater than or equal 15 to 40°C may be a homopolymer or a copolymer.

The block with a Tg of greater than or equal to 40°C may be totally or partially derived from one or more monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C.

In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have glass transition temperatures of greater than or equal to 40°C. This first block may be a homopolymer

consisting of only one type of monomer (for which the

Tg of the corresponding homopolymer is greater than or equal to  $40^{\circ}\text{C}$ ).

In the case where the first block is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is greater than or equal to 40°C. The copolymer may comprise, for example:

- monomers which are such that the homopolymers

10 prepared from these monomers have Tg values of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from

15 60°C to 120°C, and

- monomers which are such that the homopolymers prepared from these monomers have Tg values of less than 40°C, chosen from monomers with a Tg of between 20 and 40°C and/or monomers with a Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than 15°C, especially ranging from -80°C to 15°C and better still less than 10°C, for example ranging from -50°C to 0°C, as described later.

The monomers whose homopolymers have a glass transition temperature of greater than or equal to 40°C are chosen, preferably, from the following monomers,

also known as the main monomers:

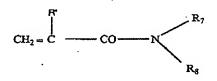
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- methacrylates of formula  $CH_2 = C(CH_3)-COOR_1$  in which  $R_1$  represents a linear or branched unsubstituted alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group or  $R_1$  represents a  $C_4$  to  $C_{12}$  cycloalkyl group,
- acrylates of formula  $CH_2$  =  $CH-COOR_2$  in which  $R_2$  represents a  $C_4$  to  $C_{12}$  cycloalkyl group such as isobornyl acrylate or a tert-butyl group,
  - (meth)acrylamides of formula:



in which R<sub>7</sub> and R<sub>8</sub>, which may be identical or different, each represent a hydrogen atom or a linear or branched C<sub>1</sub> to C<sub>12</sub> alkyl group such as an n-butyl, t-butyl, isopropyl, isohexyl, isooctyl or isononyl group; or R<sub>7</sub> represents H and R<sub>8</sub> represents a 1,1-dimethyl-3-oxobutyl group, and R' denotes H or methyl. Examples of monomers that may be mentioned include N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide,

- and mixtures thereof.

Main monomers that are particularly preferred are methyl methacrylate, isobutyl (meth)acrylate and isobornyl (meth)acrylate, and mixtures thereof.

# b) Block with a Tg of less than or equal to 20°C

The block with a Tg of less than or equal to 20°C has, for example, a Tg ranging from -100 to 20°C, preferably less than or equal to 15°C, especially ranging from -80°C to 15°C and better still less than or equal to 10°C, for example ranging from -50°C to 0°C.

The block with a Tg of less than or equal to 20°C may be a homopolymer or a copolymer.

The block with a Tg of less than or equal to 20°C may be totally or partially derived from one or more monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of less than or equal to 20°C.

In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have glass transition temperatures of less than or equal to 20°C. This second block may be a homopolymer consisting of only one type of monomer (for which the Tg of the corresponding homopolymer is less than or equal to 20°C).

In the case where the block with a Tg of less

than or equal to 20°C is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is less than or equal to 20°C.

It may comprise, for example

- one or more monomers whose corresponding homopolymer has a Tg of less than or equal to  $20\,^{\circ}\text{C}$ , for example a Tg ranging from -100 $^{\circ}\text{C}$  to  $20\,^{\circ}\text{C}$ , preferably less than
- 10 15°C, especially ranging from -80°C to 15°C and better still less than 10°C, for example ranging from -50°C to 0°C, and
  - one or more monomers whose corresponding homopolymer has a Tg of greater than  $20\,^{\circ}\text{C}$ , such as monomers with a Tg of greater than or equal to  $40\,^{\circ}\text{C}$ , for example a Tg
  - ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C and/or monomers with
- 20 a Tg of between 20 and  $40\,^{\circ}\text{C}$ , as described above.

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Preferably, the block with a Tg of less than or equal to 20°C is a homopolymer.

The monomers whose homopolymer has a Tg of less than or equal to 20°C are preferably chosen from the following monomers, or main monomer:

- acrylates of formula  $CH_2 = CHCOOR_3$ ,

 $R_3$  representing a linear or branched  $C_1$  to  $C_{12}$  unsubstituted alkyl group, with the exception of the tert-butyl group, in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated,

5 intercalated

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- methacrylates of formula  $CH_2 = C(CH_3) COOR_4$ ,  $R_4$  representing a linear or branched  $C_6$  to  $C_{12}$  unsubstituted alkyl group, in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated;
- vinyl esters of formula  $R_5\text{-}CO\text{-}O\text{-}CH = CH_2$  in which  $R_5$  represents a linear or branched  $C_4$  to  $C_{12}$  alkyl group;
  - $C_4$  to  $C_{12}$  alkyl vinyl ethers,
- 15  $N-(C_4$  to  $C_{12})$  alkyl acrylamides, such as N-octylacrylamide,
  - and mixtures thereof.

The main monomers that are particularly preferred for the block with a Tg of less than or equal to 20°C are alkyl acrylates whose alkyl chain contains from 1 to 10 carbon atoms, with the exception of the tert-butyl group, such as methyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

25 c) Block with a Tg of between 20 and 40°C

The block with a Tg of between 20 and 40°C

may be a homopolymer or a copolymer.

The block with a Tg of between 20 and 40°C may be totally or partially derived from one or more monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of between 20 and 40°C.

The block with a Tg of between 20 and 40°C may be totally or partially derived from monomers, which are such that the corresponding homopolymer has a 10 Tg of greater than or equal to 40°C and from monomers which are such that the corresponding homopolymer has a Tg of less than or equal to 20°C.

In the case where this block is a homopolymer, it is derived from monomers (or main monomer) which are such that the homopolymers prepared from these monomers have glass transition temperatures of between 20 and 40°C. This first block may be a homopolymer, consisting of only one type of monomer (for which the Tg of the corresponding homopolymer ranges from 20°C to 40°C).

The monomers whose homopolymer has a glass transition temperature of between 20 and 40°C are preferably chosen from n-butyl methacrylate, cyclodecyl acrylate, neopentyl acrylate and isodecylacrylamide, 25 and mixtures thereof.

In the case where the block with a Tg of

between 20 and 40°C is a copolymer, it is totally or partially derived from one or more monomers (or main monomer) whose nature and concentration are chosen such that the Tg of the resulting copolymer is between 20 and 40°C.

Advantageously, the block with a Tg of between 20 and 40°C is a copolymer totally or partially derived from:

- main monomers whose corresponding homopolymer has a 10 Tg of greater than or equal to 40°C, for example a Tg ranging from 40°C to 150°C, preferably greater than or equal to 50°C, for example ranging from 50 to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C, as described above, and/or - main monomers whose corresponding homopolymer has a 15 Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than or equal to 15°C, especially ranging from -80°C to 15°C and better still less than or equal to 10°C, for 20 example ranging from -50°C to 0°C, as described above, the said monomers being chosen such that the Tg of the copolymer forming the first block is between 20 and 40°C.

Such main monomers are chosen, for example,

25 from methyl methacrylate, isobornyl acrylate and

methacrylate, butyl acrylate and 2-ethylhexyl acrylate,

and mixtures thereof.

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Preferably, the proportion of the second block with a Tg of less than or equal to 20°C ranges from 10% to 85% by weight, better still from 20% to 70% and even better still from 20% to 50% by weight of the polymer.

Preferably, each of the first and second blocks comprises at least one monomer chosen from acrylic acid, acrylic acid esters, (meth)acrylic acid and (meth)acrylic acid esters, and mixtures thereof.

Advantageously, each of the first and second blocks is totally derived from at least one monomer chosen from acrylic acid, acrylic acid esters, (meth)acrylic acid and (meth)acrylic acid esters, and mixtures thereof.

However, each of the blocks may contain in small proportion at least one constituent monomer of the other block.

Thus, the first block may contain at least

20 one constituent monomer of the second block, and vice

versa.

Each of the first and/or second blocks may comprise, in addition to the monomers indicated above, one or more other monomers known as additional

25 monomers, which are different from the main monomers mentioned above.

The nature and amount of this or these additional monomer(s) are chosen such that the block in which they are present has the desired glass transition temperature.

- 5 This additional monomer is chosen, for example, from:
  - a) hydrophilic monomers such as:
  - ethylenically unsaturated monomers comprising at least one carboxylic or sulfonic acid function,
- 10 for instance:

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acrylic acid, methacrylic acid, crotonic acid,
maleic anhydride, itaconic acid, fumaric acid,
maleic acid, acrylamidopropanesulfonic acid,
vinylbenzoic acid, vinylphosphoric acid, and salts
thereof,

- ethylenically unsaturated monomers comprising at least one tertiary amine function, for instance 2-vinylpyridine, 4-vinylpyridine, dimethylamino-ethyl methacrylate, diethylaminoethyl methacrylate and dimethylaminopropylmethacrylamide, and salts thereof,
- methacrylates of formula  $CH_2 = C(CH_3)$ - $COOR_6$  in which  $R_6$  represents a linear or branched alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group, the said alkyl group being substituted with one or

more substituents chosen from hydroxyl groups (for instance 2-hydroxypropyl methacrylate and 2-hydroxyethyl methacrylate) and halogen atoms (Cl, Br, I or F), such as trifluoroethyl

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methacrylate, - methacrylates of formula  $CH_2 = C(CH_3) - COOR_9$ , R<sub>9</sub> representing a linear or branched C<sub>6</sub> to C<sub>12</sub> alkyl group in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated, the said alkyl group being substituted with one or more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F); - acrylates of formula CH<sub>2</sub> = CHCOOR<sub>10</sub>, R<sub>10</sub> representing a linear or branched C<sub>1</sub> to C<sub>12</sub> alkyl group substituted with one or more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F), such as 2-hydroxypropyl acrylate and 2-hydroxyethyl acrylate, or R<sub>10</sub> represents a C<sub>1</sub> to C<sub>12</sub> alkyl-O-POE (polyoxyethylene) with repetition of the oxyethylene unit from 5 to 30 times, for example

methoxy-POE, or R<sub>10</sub> represents a polyoxyethylenated

group comprising from 5 to 30 ethylene oxide units b) ethylenically unsaturated monomers comprising 25 one or more silicon atoms, such as methacryloxypropyltrimethoxysilane and methacryloxypropyltris(trimethylsiloxy)silane,

- and mixtures thereof.

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Additional monomers that are particularly preferred are acrylic acid, methacrylic acid and trifluoroethyl methacrylate, and mixtures thereof.

According to one embodiment, each of the first and second blocks of the block polymer comprises at least one monomer chosen from (meth)acrylic acid esters and optionally at least one additional monomer such as (meth)acrylic acid, and mixtures thereof.

According to another embodiment, each of the first and second blocks of the block polymer is totally derived from at least one monomer chosen from (meth)acrylic acid esters and optionally at least one additional monomer such as (meth)acrylic acid, and mixtures thereof.

According to one preferred embodiment, the block polymer is a non-silicone polymer, i.e. a polymer free of silicon atoms.

This or these additional monomer(s) generally represent(s) an amount of less than or equal to 30% by weight, for example from 1% to 30% by weight, preferably from 5% to 20% by weight and more preferably from 7% to 15% by weight, relative to the total weight of the first and/or second blocks.

The block polymer may be obtained by free-

radical solution polymerization according to the following preparation process:

- a portion of the polymerization solvent is introduced into a suitable reactor and heated until the adequate temperature for the polymerization is reached (typically between 60 and 120°C),
- once this temperature is reached, the constituent monomers of the first block are introduced in the presence of some of the polymerization initiator,
- after a time T corresponding to a maximum degree of conversion of 90%, the constituent monomers of the second block and the rest of the initiator are introduced,
- the mixture is left to react for a time T' (ranging from 3 to 6 hours), after which the mixture is cooled to room temperature,
- the polymer dissolved in the polymerization solvent is obtained.

## First embodiment

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According to a first embodiment, the block polymer comprises a first block with a Tg of greater than or equal to 40°C, as described above in a) and a second block with a Tg of less than or equal to 20°C, as described above in b).

Preferably, the first block with a Tg of greater than or equal to 40°C is a copolymer derived from monomers which are such that the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C, such as the monomers described above.

Advantageously, the second block with a Tg of less than or equal to 20°C is a homopolymer derived from monomers which are such that the homopolymer prepared from these monomers has a glass transition temperature of less than or equal to 20°C, such as the monomers described above.

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Preferably, the proportion of the block with a Tg of greater than or equal to 40°C ranges from 20% to 90%, better still from 30% to 80% and even better still from 50% to 70% by weight of the polymer.

Preferably, the proportion of the block with a Tg of less than or equal to 20°C ranges from 5% to 75%, preferably from 15% to 50% and better still from 25% to 45% by weight of the polymer.

Thus, according to a first variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example having a Tg ranging from 70 to 110°C, which is a methyl methacrylate/acrylic acid copolymer,

- a second block with a Tg of less than or equal to

- 20°C, for example ranging from 0 to 20°C, which is a methyl acrylate homopolymer, and
- an intermediate block which is a methyl methacrylate/acrylic acid/methyl acrylate copolymer.
- According to a second variant, the polymer according to the invention may comprise:
  - a first block with a Tg of greater than or equal to 40°C, for example ranging from 70 to 100°C, which is a methyl methacrylate/acrylic acid/trifluoroethyl
- 10 methacrylate copolymer,
  - a second block with a Tg of less than or equal to 20°C, for example ranging from 0 to 20°C, which is a methyl acrylate homopolymer, and
  - an intermediate block which is a methyl
- 15 methacrylate/acrylic acid/methyl
   acrylate/trifluoroethyl methacrylate random copolymer.

According to a third variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to
- 20 40°C, for example ranging from 85 to 115°C, which is an isobornyl acrylate/isobutyl methacrylate copolymer,
  - a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a 2-ethylhexyl acrylate homopolymer, and
- 25 an intermediate block, which is an isobornyl
   acrylate/isobutyl methacrylate/2-ethylhexyl acrylate

random copolymer.

According to a fourth variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to
- 5 40°C, for example ranging from 85 to 115°C, which is an isobornyl acrylate/methyl methacrylate copolymer,
  - a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a 2-ethylhexyl acrylate homopolymer, and
- 10 an intermediate block which is an isobornyl acrylate/methyl methacrylate/2-ethylhexyl acrylate random copolymer.

According to a fifth variant, the polymer according to the invention may comprise:

- 15 a first block with a Tg of greater than or equal to 40°C, for example ranging from 95 to 125°C, which is an isobornyl acrylate/isobornyl methacrylate copolymer,
  - a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a
- 20 2-ethylhexyl acrylate homopolymer, and
  - an intermediate block which is an isobornyl
    acrylate/isobornyl methacrylate/2-ethylhexyl acrylate
    random copolymer.

According to a sixth variant, the polymer 25 according to the invention may comprise:

- a first block with a Tg of greater than or equal to

40°C, for example ranging from 85 to 115°C, which is an isobornyl methacrylate/isobutyl methacrylate copolymer,

- a second block with a Tg of less than or equal to  $20\,^{\circ}$ C, for example ranging from -35 to -5 $^{\circ}$ C, which is an
- 5 isobutyl acrylate homopolymer, and
  - an intermediate block which is an isobornyl
    methacrylate/isobutyl methacrylate/isobutyl acrylate
    random copolymer.

According to a seventh variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 95 to 125°C, which is an isobornyl acrylate/isobornyl methacrylate copolymer,
- a second block with a Tg of less than or equal to
- 15 20°C, for example ranging from -35 to -5°C, which is an isobutyl acrylate homopolymer, and
  - an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/isobutyl acrylate random copolymer.
- According to an eighth variant, the polymer according to the invention may comprise:
  - a first block with a Tg of greater than or equal to 40°C, for example ranging from 60 to 90°C, which is an isobornyl acrylate/isobornyl methacrylate copolymer,
- 25 a second block with a Tg of less than or equal to  $20^{\circ}$ C, for example ranging from -35 to -5°C, which is an

isobutyl acrylate homopolymer, and
- an intermediate block which is an isobornyl
acrylate/isobutyl methacrylate/isobutyl acrylate random
copolymer.

5 The examples that follow illustrate, in a non-limiting manner, polymers corresponding to this first embodiment.

The amounts are expressed in grams.

#### Example 1:

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# 10 Preparation of a poly(isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate) polymer

100 g of isododecane are introduced into a
1 litre reactor and the temperature is then increased
so as to pass from room temperature (25°C) to 90°C over
1 hour.

120 g of isobornyl acrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at  $90^{\circ}\text{C}$  for 1 hour 30 minutes.

90 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-25 peroxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

The mixture is maintained at  $90\,^{\circ}\text{C}$  for 3 hours and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobutyl methacrylate) first block with a Tg of 80°C, a poly-2-ethylhexyl acrylate second block with a Tg of -70°C and an intermediate block that is an isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 77 000 and a number-average mass of 19 000, i.e. a polydispersity index I of 4.05.

### Example 2:

# Preparation of a poly(isobornyl acrylate/isobornyl methacrylate/2-ethylhexyl acrylate) polymer

100 g of isododecane are introduced into a

1 litre reactor and the temperature is then increased
so as to pass from room temperature (25°C) to 90°C over
20 1 hour.

105 g of isobornyl acrylate, 105 g of isobornyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

The mixture is maintained at 90°C for 1 hour

30 minutes.

90 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

The mixture is maintained at  $90^{\circ}\text{C}$  for 3 hours and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobornyl methacrylate) first block with a Tg of 110°C, a poly-2-ethylhexyl acrylate second block with a Tg of -70°C and an intermediate block that is an isobornyl acrylate/isobornyl methacrylate/2-ethylhexyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 103 900 and a number-average mass of 21 300, i.e. a polydispersity index I of 4.89.

#### Example 3:

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# 20 Preparation of a poly(isobornyl acrylate/isobutyl methacrylate/isobutyl acrylate) polymer

100 g of isododecane are introduced into a

1 litre reactor and the temperature is then increased
so as to pass from room temperature (25°C) to 90°C over
1 hour.

120 g of isobornyl acrylate, 90 g of isobutyl

methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added, at 90°C and over 1 hour.

5 The mixture is maintained at 90°C for 1 hour 30 minutes.

90 g of isobutyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane are then introduced into the above mixture, still at 90°C and over 30 minutes.

The mixture is maintained at 90°C for 3 hours and is then cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobutyl methacrylate) first block with a Tg of 75°C, a polyisobutyl acrylate second block with a Tg of -20°C and an intermediate block that is an isobornyl acrylate/isobutyl methacrylate/isobutyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 144 200 and a number-average mass of 49 300, i.e. a polydispersity index I of 2.93.

### Second embodiment

According to a second embodiment, the block polymer comprises a first block having a glass

transition temperature (Tg) of between 20 and 40°C, in accordance with the blocks described in c) and a second block having a glass transition temperature of less than or equal to 20°C, as described above in b) or a glass transition temperature of greater than or equal to 40°C, as described in a) above.

Preferably, the proportion of the first block with a Tg of between 20 and 40°C ranges from 10% to 85%, better still from 30% to 80% and even better still from 50% to 70% by weight of the polymer.

When the second block is a block with a Tg of greater than or equal to 40°C, it is preferably present in a proportion ranging from 10% to 85% by weight, better still from 20% to 70% and even better still from 30% to 70% by weight of the polymer.

When the second block is a block with a Tg of less than or equal to 20°C, it is preferably present in a proportion ranging from 10% to 85% by weight, better still from 20% to 70% and even better still from 20% to 50% by weight of the polymer.

20

Preferably, the first block with a Tg of between 20 and 40°C is a copolymer derived from monomers which are such that the corresponding homopolymer has a Tg of greater than or equal to 40°C, and from monomers which are such that the corresponding homopolymer has a Tg of less than or equal to 20°C.

Advantageously, the second block with a Tg of less than or equal to  $20\,^{\circ}\text{C}$  or with a Tg of greater than or equal to  $40\,^{\circ}\text{C}$  is a homopolymer.

Thus, according to a first variant of this

- 5 second embodiment, the block polymer may comprise:
  - a first block with a Tg of between 20 and 40°C, for example with a Tg of 25 to 39°C, which is a copolymer comprising at least one methyl acrylate monomer, at least one methyl methacrylate monomer and at least one acrylic acid monomer,
  - a second block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 125°C, which is a homopolymer composed of methyl methacrylate monomers, and
- an intermediate block comprising at least one methyl acrylate, methyl methacrylate monomer, and
   an intermediate block comprising methyl methacrylate, at least one acrylic acid monomer and at least one
- 20 According to a second variant of this second embodiment, the block polymer may comprise:
  - a first block with a Tg of between 20 and 40°C, for example with a Tg of 21 to 39°C, which is a copolymer comprising isobornyl acrylate/isobutyl
- 25 methacrylate/2-ethylhexyl acrylate,

methyl acrylate monomer.

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- a second block with a Tg of less than or equal to

20°C, for example ranging from -65 to -35°C, which is a methyl methacrylate homopolymer, and

- an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate5 random copolymer.
  - According to a third variant of this second embodiment, the block polymer may comprise:
  - a first block with a Tg of between 20 and 40°C, for example with a Tg from 21 to 39°C, which is an
- 10 isobornyl acrylate/methyl acrylate/acrylic acid
   copolymer,
  - a second block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 115°C, which is an isobornyl acrylate homopolymer, and
- 15 an intermediate block which is an isobornyl acrylate/methyl acrylate/acrylic acid random copolymer.

The composition according to the invention preferably contains from 0.1% to 60% by weight of active material (or solids), preferably from 0.5% to 50% by weight and more preferably from 1% to 40% by weight, of the polymer.

The composition according to the invention may comprise a hydrophilic medium comprising water or a mixture of water and of hydrophilic organic solvent(s),

25 for instance alcohols and especially linear or branched lower monoalcohols containing from 2 to 5 carbon atoms,

for instance ethanol, isopropanol or n-propanol, and polyols, for instance glycerol, diglycerol, propylene glycol, sorbitol, pentylene glycol and polyethylene glycols, or alternatively hydrophilic C<sub>2</sub> ethers and C<sub>2</sub>-5 C<sub>4</sub> aldehydes.

The water or the mixture of water and of hydrophilic organic solvents may be present in the composition according to the invention in a content ranging from 0.1% to 99% by weight and preferably from 10% to 80% by weight relative to the total weight of the composition.

10

The composition according to the invention comprises a cosmetically acceptable organic liquid medium (acceptable tolerance, toxicology and feel).

- According to one particularly preferred embodiment, the organic liquid medium of the composition contains at least one organic solvent, which is the or one of the polymerization solvent(s) for the block polymer as described above.
- 20 Advantageously, the said organic solvent is the liquid that is in majority amount by weight in the organic liquid medium of the cosmetic composition.

According to one embodiment, the organic liquid medium comprises fatty substances that are liquid at room temperature (in general 25°C). These liquid fatty substances may be of animal, plant,

mineral or synthetic origin.

As fatty substances that are liquid at room temperature, often known as oils, which may be used in the invention, mention may be made of: hydrocarbon-5 based oils of animal origin such as perhydrosqualene; hydrocarbon-based plant oils such as liquid triglycerides of fatty acids containing from 4 to 10 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively sunflower oil, corn 10 oil, soybean oil, grapeseed oil, sesame seed oil, apricot oil, macadamia oil, castor oil, avocado oil, caprylic/capric acid triglycerides, jojoba oil or shea butter; linear or branched hydrocarbons, of mineral or synthetic origin, such as liquid paraffins and derivatives thereof, petroleum jelly, polydecenes, and hydrogenated polyisobutylene such as parleam; synthetic esters and ethers, especially of fatty acids, for instance purcellin oil, isopropyl myristate, 2ethylhexyl palmitate, 2-octyldodecyl stearate, 2-20 octyldodecyl erucate or isostearyl isostearate; hydroxylated esters, for instance isostearyl lactate, octyl hydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate, and fatty alkyl heptanoates, octanoates or decanoates; polyol 25 esters, for instance propylene glycol dioctanoate,

neopentyl glycol diheptanoate or diethylene glycol

diisononanoate; and pentaerythritol esters; fatty
alcohols containing from 12 to 26 carbon atoms, for
instance octyldodecanol, 2-butyloctanol, 2hexyldecanol, 2-undecylpentadecanol or oleyl alcohol;

5 partially hydrocarbon-based and/or partially siliconebased fluoro oils; silicone oils, for instance volatile
or non-volatile, linear or cyclic polymethylsiloxanes
(PDMS), for instance cyclomethicones, dimethicones
optionally comprising a phenyl group, for instance

10 phenyl trimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenyl dimethyl dimethyl
trisiloxanes, diphenyl dimethicones, phenyl
dimethicones and polymethyl phenylsiloxanes; mixtures
thereof.

These oils may be present in a content ranging from 0.01% to 90% and better still from 0.1% to 85% by weight relative to the total weight of the composition.

The organic liquid medium of the composition

20 according to the invention may also comprise one or

more cosmetically acceptable organic solvents

(acceptable tolerance, toxicology and feel).

These solvents may generally be present in a content ranging from 0.1% to 90%, preferably from 10% to 90% and better still from 30% to 90% by weight relative to the total weight of the composition.

25

As solvents that may be used in the composition of the invention, mention may be made, besides the hydrophilic organic solvents mentioned above, of ketones that are liquid at room temperature, 5 such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone and acetone; propylene glycol ethers that are liquid at room temperature, such as propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate and 10 dipropylene glycol mono-n-butyl ether; short-chain esters (containing from 3 to 8 carbon atoms in total), such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate and isopentyl acetate; ethers that are liquid at room temperature, such as diethyl ether, 15 dimethyl ether and dichlorodiethyl ether; alkanes that are liquid at room temperature, such as decane, heptane, dodecane, isododecane and cyclohexane; cyclic aromatic compounds that are liquid at room temperature, such as toluene and xylene; aldehydes that are liquid 20 at room temperature, such as benzaldehyde and acetaldehyde, and mixtures thereof.

The composition may comprise, besides the block polymer described above an additional polymer such as a film-forming polymer. According to the present invention, the term "film-forming polymer" means a polymer that is capable of forming, by itself

or in the presence of an auxiliary film-forming agent, a continuous film that adheres to a support, especially to keratin materials.

Among the film-forming polymers that may be

5 used in the composition of the present invention,
mention may be made of synthetic polymers, of freeradical type or of polycondensate type, polymers of
natural origin, and mixtures thereof. Film-forming
polymers that may be mentioned in particular include

10 acrylic polymers, polyurethanes, polyesters,
polyamides, polyureas and cellulose-based polymers, for
instance nitrocellulose.

The polymer may be combined with one or more auxiliary film-forming agents. Such a film-forming agent may be chosen from any compound known to those skilled in the art as being capable of fulfilling the desired function, and may be chosen especially from plasticizers and coalescers.

The composition according to the invention

20 may comprise at least one wax. For the purposes of the

present invention, the term "wax" means a lipophilic

compound that is solid at room temperature (25°C),

which undergoes a reversible solid/liquid change of

state, and which has a melting point of greater than or

25 equal to 30°C, which may be up to 120°C.

The melting point of the wax may be measured

using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name DSC 30 by the company Mettler.

The waxes may be hydrocarbon-based waxes,

fluoro waxes and/or silicone waxes and may be of plant,
mineral, animal and/or synthetic origin. In particular,
the waxes have a melting point of greater than 25°C and
better still greater than 45°C.

As waxes that may be used in the composition

of the invention, mention may be made of beeswax,

carnauba wax or candelilla wax, paraffin, microcrystal
line waxes, ceresin or ozokerite, synthetic waxes, for

instance polyethylene waxes or Fischer-Tropsch waxes,

and silicone waxes, for instance alkyl or alkoxy

dimethicones containing from 16 to 45 carbon atoms.

The nature and amount of the solid fatty substances depend on the desired mechanical properties and textures. As a guide, the composition may contain from 0 to 50% by weight and better still from 1% to 30% by weight of waxes, relative to the total weight of the composition.

The composition according to the invention may also comprise one or more dyestuffs chosen from water-soluble dyes and pulverulent dyestuffs, for instance pigments, nacres and flakes that are well known to those skilled in the art. The dyestuffs may be

present in the composition in a content ranging from 0.01% to 50% by weight and preferably from 0.01% to 30% by weight, relative to the weight of the composition.

The term "pigments" should be understood as

5 meaning white or coloured, mineral or organic particles
of any shape, which are insoluble in the physiological
medium and which are intended to colour the
composition.

The term "nacres" should be understood as meaning iridescent particles of any shape, produced especially by certain molluscs in their shell, or alternatively synthesized.

The pigments may be white or coloured, and mineral and/or organic. Among the mineral pigments that 15 may be mentioned are titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders,

for instance aluminium powder or copper powder.

Among the organic pigments that may be mentioned are carbon black, pigments of D & C type, and lakes based on cochineal carmine or on barium, strontium, calcium or aluminium.

25 Mention may also be made of pigments with an effect, such as particles comprising a natural or

synthetic, organic or mineral substrate, for example glass, acrylic resins, polyester, polyurethane, polyethylene terephthalate, ceramics or aluminas, the said substrate being uncoated or coated with metal substances, for instance aluminium, gold, silver, platinum, copper or bronze, or with metal oxides, for instance titanium dioxide, iron oxide or chromium oxide, and mixtures thereof.

The nacreous pigments may be chosen from

white nacreous pigments such as mica coated with

titanium or with bismuth oxychloride, coloured nacreous

pigments such as titanium mica coated with iron oxides,

titanium mica coated especially with ferric blue or

chromium oxide, titanium mica coated with an organic

pigment of the abovementioned type and also nacreous

pigments based on bismuth oxychloride. Interference

pigments, especially liquid-crystal pigments or

multilayer pigments, may also be used.

The water-soluble dyes are, for example,
20 beetroot juice or methylene blue.

The composition according to the invention may also comprise one or more fillers, especially in a content ranging from 0.01% to 50% by weight and preferably ranging from 0.01% to 30% by weight,

25 relative to the total weight of the composition. The term "fillers" should be understood as meaning

colourless or white, mineral or synthetic particles of any shape, which are insoluble in the medium of the composition, irrespective of the temperature at which the composition is manufactured. These fillers serve especially to modify the rheology or the texture of the composition.

The fillers may be mineral or organic in any form, platelet-shaped, spherical or oblong, irrespective of the crystallographic form (for example leaflet, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide (Nylon®) powders (Orgasol® from Atochem), poly- $\beta$ alanine powder and polyethylene powder, powders of tetrafluoroethylene polymers (Teflon®), lauroyllysine, starch, boron nitride, hollow polymer microspheres such as those of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industrie) or acrylic acid copolymers (Polytrap® from the company Dow Corning) and silicone resin microbeads (for example Tospearls® from Toshiba), elastomeric polyorganosiloxane particles, 20 precipitated calcium carbonate, magnesium carbonate, magnesium hydrocarbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, and metal soaps derived from 25 organic carboxylic acids containing from 8 to 22 carbon

atoms and preferably from 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc laurate or magnesium myristate.

The composition according to the invention

5 may especially be in the form of a stick, a suspension, a dispersion, a solution, a gel, an emulsion, especially an oil-in-water (O/W) emulsion, a water-in-oil (W/O) emulsion or a multiple emulsion (W/O/W or polyol/O/W or O/W/O emulsion), in the form of a cream,

10 a paste, a mousse, a dispersion of vesicles, especially of ionic or nonionic lipids, a two-phase or multi-phase lotion, a spray, a powder, a paste, especially a soft paste (especially a paste with a dynamic viscosity at 25°C of about from 0.1 to 40 Pa.s under a shear rate of 200 s<sup>-1</sup>, after measurement for 10 minutes in cone/plate geometry). The composition may be anhydrous; for example, it may be an anhydrous paste.

A person skilled in the art may select the appropriate galenical form, and also the method for 20 preparing it, on the basis of his general knowledge, taking into account firstly the nature of the constituents used, especially their solubility in the support, and secondly the intended application for the composition.

The composition according to the invention may be a makeup composition, for instance products for

the complexion (foundations), makeup rouges,
eyeshadows, lipsticks, concealer products, blushers,
mascaras, eyeliners, eyebrow makeup products, lip or
eye pencils, nail products, such as nail varnishes,
body makeup products or hair makeup products (hair
mascara or hair lacquer).

The composition according to the invention may also be a care product for body and facial skin, especially an antisun product or a skin-colouring product (such as a self-tanning product).

The composition according to the invention may also be a haircare product, especially for holding or styling the hair or for shaping the hair. The haircare compositions are preferably shampoos,

15 hairsetting gels or lotions, blow-drying lotions, or fixing and styling compositions such as lacquers or sprays.

A subject of the present invention is also a cosmetic assembly comprising:

- 20 a container delimiting at least one compartment, the said container being closed by a closing member; and
  - a composition as described above placed inside the said compartment.
- 25 The container may be in any adequate form. It may especially be in the form of a bottle, a tube, a

The closing member may be in the form of a

jar, a case, a box, a sachet or a carton.

removable stopper, a lid, a cap, a tear-off strip or a capsule, especially of the type comprising a body attached to the container and a cover cap articulated on the body. It may also be in the form of a member for selectively closing the container, especially a pump, a valve or a flap valve.

The container may be combined with an 10 applicator, especially in the form of a brush comprising an arrangement of bristles maintained by a twisted wire. Such a twisted brush is described especially in patent US 4 887 622. It may also be in the form of a comb comprising a plurality of application members, obtained especially by moulding. Such combs are described, for example, in patent FR 2 796 529. The applicator may be in the form of a fine brush, as described, for example, in patent FR 2 722 380. The applicator may be in the form of a 20 block of foam or of elastomer, a felt or a spatula. The applicator may be free (tuft or sponge) or securely fastened to a rod borne by the closing member, as described, for example, in patent US 5 492 426. The

The product may be contained directly in the

applicator may be securely fastened to the container,

as described, for example, in patent FR 2 761 959.

container, or indirectly. By way of example, the product may be arranged on an impregnated support, especially in the form of a wipe or a pad, and arranged (individually or in plurality) in a box or in a sachet.

5 Such a support incorporating the product is described, for example, in patent application WO 01/03538.

The closing member may be coupled to the container by screwing. Alternatively, the coupling between the closing member and the container is done other than by screwing, especially via a bayonet mechanism, by click-fastening, gripping, welding, bonding or by magnetic attraction. The term "click-fastening" in particular means any system involving the crossing of a bead or cord of material by elastic deformation of a portion, especially of the closing member, followed by return to the elastically unconstrained position of the said portion after the crossing of the bead or cord.

The container may be at least partially made

20 of thermoplastic material. Examples of thermoplastic

materials that may be mentioned include polypropylene

or polyethylene.

Alternatively, the container is made of non-thermoplastic material, especially glass or metal (or alloy).

25

The container may have rigid walls or

deformable walls, especially in the form of a tube or a tubular bottle.

The container may comprise means for distributing or facilitating the distribution of the 5 composition. By way of example, the container may have deformable walls so as to allow the composition to exit in response to a positive pressure inside the container, this positive pressure being caused by elastic (or non-elastic) squeezing of the walls of the container. Alternatively, especially when the product 10 is in the form of a stick, the product may be driven out by a piston mechanism. Still in the case of a stick, especially of makeup product (lipstick, foundation, etc.), the container may comprise a 15 mechanism, especially a rack mechanism, a threaded-rod mechanism or a helical groove mechanism, and may be capable of moving a stick in the direction of the said aperture. Such a mechanism is described, for example, in patent FR 2 806 273 or in patent FR 2 775 566. Such 20 a mechanism for a liquid product is described in patent FR 2 727 609.

The container may consist of a carton with a base delimiting at least one housing containing the composition, and a lid, especially articulated on the base, and capable of at least partially covering the said base. Such a carton is described, for example, in

patent application WO 03/018423 or in patent FR 2 791 042.

The container may be equipped with a drainer arranged in the region of the aperture of the

5 container. Such a drainer makes it possible to wipe the applicator and possibly the rod to which it may be securely fastened. Such a drainer is described, for example, in patent FR 2 792 618.

The composition may be at atmospheric

10 pressure inside the container (at room temperature) or pressurized, especially by means of a propellent gas (aerosol). In the latter case, the container is equipped with a valve (of the type used for aerosols).

The content of the patents or patent

15 applications mentioned above are incorporated by reference into the present patent application.

The examples that follow illustrate the compositions according to the invention in a non-limiting manner.

#### 20 Example 4: Lipstick

The percentages are expressed on a weight basis.

Polymer of Example 3	90.7
Hydrogenated polyisobutene	2.1
Octyldodecanol	0.9

Phenyl trimethicone	2.1
(DC 556, 20 cSt, Dow Corning)	
Copolymer vinylpyrrolidone/1-eicosene	1.2
(Antaron V-220, ISP)	
Pigments	3

#### Procedure

- A ground pigmentary mixture of the pigments in the oily phase is prepared by treating the mixture three times in a three-roll mill.
- 2. The ground material required for the composition and the other ingredients are weighed out in a beaker.
- 3. The mixture is stirred using a Rayneri blender for 45 minutes at room temperature.
- 10 4. The formula is cast in isododecane-leaktight cooling boxes.

## Gloss measurement

- 1. A film with a wet thickness of 50 µm are prepared
   using a mechanical applicator. The depositions are made on a LENETA contrast card with the reference
   FORM 1A PENOPAC.
  - 2. The film is left to dry for 24 hours at a regulated temperature of  $30\,^{\circ}\text{C}$ .
- 20 3. The gloss measurements are performed using a Byk Gardner micro-tri-gloss glossmeter with measuring

angles of 20° and 60°.

The in vitro gloss results obtained are given in the table below:

Angle	Composition whose gloss is	Mean	Standard
	measured	(웅)	deviation
20°	Pigmented composition of the	0.8	0.8
	product Lipfinity		
20°	Example 4	46.2	1.9
60°	Pigmented composition of the	6.5	1.1
	product Lipfinity		
60°	Example 4	74.5	1.5

5 The product Lipfinity is a lip makeup product comprising a pigmented liquid lipstick and a transparent colourless balm in the form of a stick. The gloss and transfer measurements were performed on the pigmented liquid lipstick composition of the product sold under the brand name Lipfinity.

The transfer index is measured according to the method described above.

Product whose transfer	Transfer value
index is evaluated	(in %)
Pigmented composition of	1.4 ± 0.1
the product Lipfinity	
Example 4	1.3 ± 0.9

### Example 5: Mascara composition

Beeswax	8 g
Paraffin wax	3 g
Carnauba wax	6 g
Hectorite modified with distearyldimethylbenzyl-	5.3 g
ammonium chloride (Bentone® 38V from Elementis)	
Propylene carbonate	1.7 g
Filler	1 g
Pigments	5 g
Polymer of Example 1	12 g AN
Isododecane	qs 100
Example 6: Mascara composition	
Beeswax	8 g
Paraffin wax	3 g
Carnauba wax	6 g
Hectorite modified with distearyldimethylbenzyl-	5.3 g
ammonium chloride (Bentone® 38V from Elementis)	
Propylene carbonate	1.7 g
Filler	1 g
Pigments	5 g
Polymer of Example 2	12 g AM

qs 100

Isododecane